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Quenching of $N_2(a^1\Pi_g, v'=0)$ by N_2 , O_2 , CO , CO_2 , CH_4 , H_2 , and Ar

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* William J. Marinelli, * William J. Kessler, * Byron David Green, * and William A.M. Blumberg

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William A.M. Blumberg

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William J. Marinelli, William J. Kessler, and Byron David Green
Physical Sciences, Inc., Research Park, P.O. Box 3100, Andover, Massachusetts 01810

William A. M. Blumberg
Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts 01731

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William J. Marinelli, William J. Kessler, and Byron David Green
Physical Sciences, Inc., Research Park, P.O. Box 3100, Andover, Massachusetts 01810

William A. M. Blumberg
Air Force Geophysics Laboratory, Hanscomb AFB, Massachusetts 01731

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We have determined quenching rate coefficients for N₂(a' $^1\Pi_g$, v' = 0) by N₂, O₂, H₂, CO₂, Ar, CH₄, and CO using two-photon laser excitation. Quenching by N₂ appears to proceed via collisional coupling to N₂(a' $^1\Sigma_u^-$, v = 0) with a rate coefficient of $2.2 \pm 0.2 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Quenching by Ar is nearly as efficient. Gas-kinetic rate coefficients are obtained for quenching by CO, O₂, H₂, CO₂, and CH₄. Collisional energy transfer from N₂(a, 0) to CO(A) is observed in these experiments. However, quenching by O₂, H₂, CO₂, and CH₄ is thought to be reactive.

I. INTRODUCTION

One of the most examined areas in molecular energy transfer is the exchange of energy between near-resonant states in different molecules. Extensive experimental and theoretical attention has been given to the atom-atom and atom-diatom transfer processes. Electronic-to-vibrational energy transfer in atom-diatom and diatom-diatom collisions has also been intensively investigated. A much less well investigated area is the competition between radiative, intramolecular, and intermolecular electronic relaxation processes. A theoretical treatment of such processes is complex, since information about two electronic potential curves and the intermolecular interaction potential must be available. Nonetheless, studies of such processes are extremely important, especially when the excited state is metastable and may act as an energy storage reservoir. These states may play an important role in chemical laser kinetics, atmospheric background emissions, and plasma kinetics.

An example of such a coupled system is found in the lowest lying singlet states of N₂. The a' $^1\Pi_g$, a' $^1\Sigma_u^-$, and w' $^1\Delta_u$ states all have term energies of approximately 8.5 eV and are metastable with respect to radiation to the ground X $^1\Sigma_g^+$ state. An electronic energy level diagram of these states, shown in Fig. 1, highlights the many opportunities for near-resonant energy exchange within the singlet manifold.

These states may be coupled via emission of infrared radiation. The w-a and a'-a transitions comprise the well known McFarlane infrared transitions in N₂. These transitions were observed in N₂ laser cavities by McFarlane¹ and the w-a transition has been most recently observed by Fraser, Rawlins, and Miller.² The a-a' transition has been recently probed in absorption using diode laser spectroscopy by Hirota.³ Transition probabilities for the a-a' transition have been calculated by Freund⁴ and have recently been refined by Marinelli, Green, DeFaccio, and Blumberg.⁵ Radiative coupling of these states to the ground state is via forbidden transitions. The well known a' $^1\Pi_g$ -X $^1\Sigma_g^+$ (Lyman-Birge-Hopfield) bands have been the subject of numerous studies,⁶ although the radiative lifetime of the a' $^1\Pi_g$ state remains a subject of much controversy. Measurements

of the lifetime center around a value of $80^{+40}_{-20} \mu\text{s}$.⁷⁻¹⁰ The a' $^1\Sigma_u^-$ -X $^1\Sigma_g^+$ transition (Ogawa-Tanaka-Wilkinson-Mulliken bands) have been observed in absorption. Only v' = 0 of this state has been observed in emission.^{5,6} The radiative lifetime of the a' $^1\Sigma_u^-$ state is also quite uncertain and varies strongly with rotational level,^{11,12} although the latest work of Piper¹³ appears to have established a lower bound on the average lifetime of 23^{+11}_{-6} ms. The w' $^1\Delta_u$ -X $^1\Sigma_g^+$ transition has only been observed in absorption in high pressure N₂.⁶

The collisional relaxation of the coupled singlet states has been investigated in a series of papers by Golde and Thrush,¹⁴⁻¹⁷ Freund,⁴ van Veen and co-workers,¹⁸ and Piper.¹³ Collisional quenching of the a' $^1\Pi_g$ state by CO has been investigated by Filseth¹⁹ and Sha, Proch, and Kompa.²⁰ Rotational relaxation of the a' $^1\Pi_g$ state has also been investigated by Kompa and co-workers.²¹ Most recently, vibrational

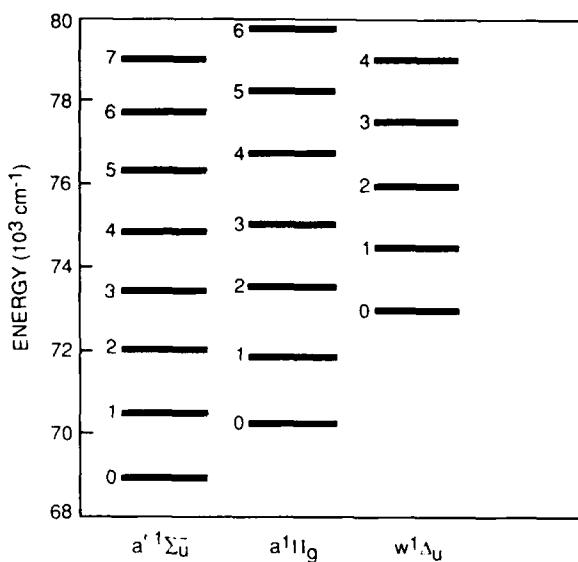
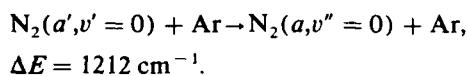


FIG. 1. Ladder diagram of low-lying N₂ singlet states.

relaxation of N₂(*a*) and intersystem crossing with the *a'* state has been investigated by Marinelli, Green, DeFaccio, and Blumberg.⁵

The early work by Golde and Thrush used a discharge flow reactor to create active nitrogen in Ar at pressures from 1–6 Torr. Their observation of *a'-X* and *a-X* emissions showed that N₂(*a*, *v* = 0) could be excited by N₂(*a'*, *v* = 0) through the endoergic process



This conclusion was supported by the observed variation in *a'/a* emission intensities with pressure and temperature. They measured electronic quenching of N₂(*a*, *v* = 0) by Ar and N₂ to be slow ($k_{\text{Ar}} \sim 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{N}_2} = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).^{15,17} The quenching rate coefficient for CO₂ was measured to be approximately $6.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and was independent of the *a*-state vibrational level.

Golde and Thrush also observed the quenching rates of high vibrational levels of N₂(*a*) by N₂ to be strongly dependent on both vibrational level and temperature. The high levels of the *a* state were produced via N-atom recombination. They measured quenching rate coefficients ranging from 1.6×10^{-12} to $2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for vibrational levels 0–6. Quenching by Ar was observed to have similar rates, suggesting that little energy is transferred in the process and that transfer to the *a'* and/or *w* states is the dominant quenching mechanism.

Direct two-photon excitation of N₂(*a*, *v*' = 0,1) was used by van Veen and co-workers¹⁸ in their quenching studies. They observed both simple quenching of the *a* state at low pressures and coupled relaxation of the *a-a'* states at higher pressures. Quenching rate coefficients of 2.1×10^{-11} and $2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were measured for N₂(*a*) levels 0 and 1, respectively. At higher pressures a decay rate coefficient of $2.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was measured for the coupled system. They concluded that this rate was due to the rate-limiting relaxation of N₂(*a*, *v* = 0).

The latter conclusion is supported by the measurements of Piper.¹³ In his study of N₂(*a'*) quenching by a range of gases he measured a rate coefficient for relaxation by N₂ of $1.9 \pm 0.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Quenching by NO, CH₄, CO, and N₂O was observed to be approximately gas kinetic while quenching by H₂, O₂, and CO₂ was observed to be roughly a tenth gas kinetic. Quenching by Ar was observed to be quite slow ($k \ll 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).¹³ Quenching by CO was observed to efficiently produce CO(*A-X*) emission. Energy transfer from N₂(*a*) to CO was also observed to produce *A-X* emission by Kompa and co-workers.²⁰ They measured a quenching rate coefficient a factor of 3–4 greater than gas kinetic for the total relaxation process. The energy mismatch between N₂(*a*) and CO(*A*) vibrational levels was observed to be the controlling factor in the partitioning of energy to CO(*A,v*).

Quenching of high vibrational levels of N₂(*a*) by N₂ was observed to be nearly gas kinetic by Marinelli and co-workers.⁵ The lower vibrational levels were measured to re-

lax at rates nearly one-tenth gas kinetic but coupling to the *a'* state in their electron-beam excitation experiment made an exact determination of these rate coefficients quite difficult. Electronic relaxation of the vibrational manifold was measured to have an average rate coefficient of $8.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, somewhat lower than the results for *v* = 0,1 measured by van Veen *et al.*¹⁸

This present study extends our previous work. We now use two-photon excitation of N₂(*a*, *v* = 0) to examine quenching of this level by a variety of species. Our hope is to provide more detailed insight into the global observations of the previous study.

II. EXPERIMENTAL

These experiments were conducted using a standard laser-induced fluorescence apparatus consisting of a flow cell, Nd:YAG pumped dye laser system, and time-resolved fluorescence detection equipment. A schematic diagram of the apparatus is shown in Fig. 2 and each of the components is described in detail below.

The quenching experiments were performed in a 2.5 cm diameter flow reactor pumped by a 17 cfm rotary pump. Flow velocities in excess of 1000 cm s⁻¹ are achieved in this system. A flowing system was employed to eliminate the possibility of interference in the kinetic measurements due to quenching by laser produced species or reaction products. Flow rates for N₂ and other quenching species were measured using calibrated mass flow meters (Teledyne-Hastings) and total cell pressures were determined using capacitance manometers (MKS Instruments). All gases were standard reagent grade and were used without further purification. The kinetic measurements were performed in a section of the flow reactor consisting of a Teflon coated (DuPont Poly TFE) and internally-blackened six-way cross. One axis of the cross was utilized for gas flow while a second axis was equipped with baffled S1-UV quartz windows for introduction of the laser beam. The third axis of the cross was fitted with a photomultiplier tube (PMT) to view the fluorescence.

The N₂(*a* 1Π_g, *v*' = 0) state was excited using a pulsed Nd:YAG pumped dye laser (Quanta International YG

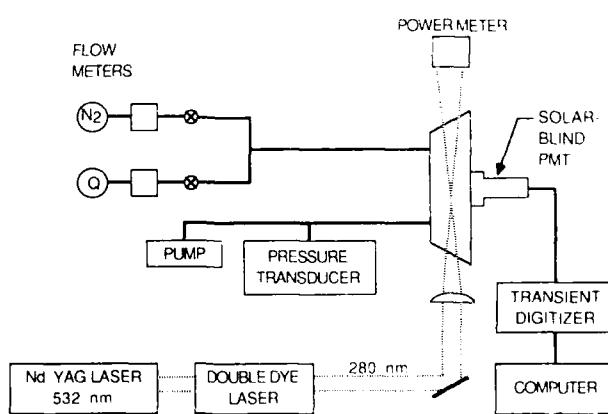


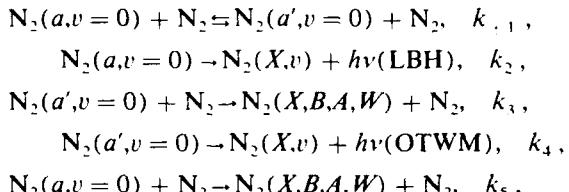
FIG. 2. Schematic diagram of experimental apparatus used in quenching experiments.

581C/TDL 50). The output from a 50% mixture of R590/R610 was frequency doubled to obtain approximately 10 mJ at 290 nm in a 7 ns Q-switched pulse. The UV output of the laser system was maximized using servo tracking of the nonlinear KDP crystal phase matching angle. A Pellin-Brocha prism was used to separate the fundamental and second harmonic output of the laser system. Right-angle prisms were used to direct the beam to a 10 cm focal length S1-UV quartz lens which focused it to a spot in the center of the cell. The laser power was monitored at the exit window of the cell using a surface-absorbing power meter (Scientech).

Fluorescence was observed from the N₂(a-X) transition using a solar-blind PMT (EMR 542G-17) located approximately 6 cm from the laser focal volume. A flow of N₂ was used to purge the region between the CaF₂ window of the fluorescence cell and the PMT photocathode. This technique has been shown to effectively eliminate O₂ absorption at wavelengths above 145 nm. No fluorescence collection optics were employed (effective *f*/3.2) and the distance from the center of the cell to the exit window was limited to 4 cm to minimize absorption of fluorescence by some of the quenching gases. Fluorescence signals from the PMT were captured using a 200 MHz transient digitizer and stored on an IBM-PC for analysis (LeCroy TR8828C/CATALYST). A standard linear least-squares analysis package was employed to obtain kinetic rates from the fluorescence decays.

III. RESULTS AND ANALYSIS

Quenching of N₂(a, v = 0) is complicated by the possibility of collisional coupling to N₂(a', v'' = 0). For the case of quenching by N₂ the relevant kinetic processes are described by



where creation of N₂(a, v' = 0) by the laser occurs on a time scale rapid compared with relaxation. Energy transfer from a(0) to a'(1) has not been included in this analysis. The process is 295 cm⁻¹ endoergic. There is no evidence in the data for coupling of these levels. The rate equations describing relaxation of N₂(a, v = 0) are given by

$$\begin{aligned} \frac{d[\text{N}_2(a)]}{dt} = -\{ &(k_1 + k_5)[\text{N}_2] + k_2\}[\text{N}_2(a)] \\ &+ k_{11}[\text{N}_2(a')][\text{N}_2], \end{aligned} \quad (1)$$

where

$$\begin{aligned} \frac{d[\text{N}_2(a')]}{dt} = -\{ &(k_{-1} + k_3)[\text{N}_2] + k_4\}[\text{N}_2(a')] \\ &+ k_1[\text{N}_2(a)][\text{N}_2]. \end{aligned} \quad (2)$$

The treatment of this coupled system, neglecting activation from the ground state, has been reviewed for the case of vibrational energy transfer by Yardley.²² The solution to these equations for the behavior of N₂(a, v = 0) is given by

$$\begin{aligned} [\text{N}_2(a)]_t = [\text{N}_2(a)]_0 &\left[\frac{(\lambda_2 - C_{11})}{\lambda_2 - \lambda_1} e^{-\lambda_1 t} \right. \\ &\left. + \frac{(C_{11} - \lambda_1)}{\lambda_2 - \lambda_1} e^{-\lambda_2 t} \right], \end{aligned} \quad (3)$$

where

$$C_{11} = (k_1 + k_5)[\text{N}_2] + k_2,$$

$$C_{12} = k_{-1}[\text{N}_2],$$

$$C_{21} = k_1[\text{N}_2],$$

$$C_{22} = (k_{-1} + k_3)[\text{N}_2] + k_4.$$

The two decay constants, λ_1 and λ_2 , are given by the relations

$$\begin{aligned} \lambda_1, \lambda_2 = -\frac{1}{2}\{ &(C_{11} + C_{22}) \pm [(C_{11} + C_{22})^2 \\ &- 4(C_{11}C_{22} - C_{12}C_{21})]^{1/2}\}, \end{aligned} \quad (4)$$

$$\lambda_1\lambda_2 = C_{11}C_{22} - C_{12}C_{21}, \quad (5)$$

$$\lambda_1 + \lambda_2 = C_{22} + C_{11}. \quad (6)$$

In our experiments, N₂(a, v = 0) is produced by the laser and decays initially to reach a coupled equilibrium with N₂(a', v = 0). The system subsequently decays at a rate determined by a weighted average of the relaxation rates to the ground or other excited states. The weighting factor is simply the Boltzmann distribution of total population in N₂(a) and N₂(a'). An additional relation between λ_1 and λ_2 gives the ratio of the amplitude components of the fast (initial) and slow (final) decays; S:

$$S = \frac{\lambda_2 - C_{11}}{C_{11} - \lambda_1}. \quad (7)$$

For the coupled system N₂(a, v = 0)/N₂(a', v = 0) the amplitude ratio is given by

$$S = \left(\frac{k_1}{k_{-1}} \right) \left(\frac{k_5[\text{N}_2] + k_2}{k_3[\text{N}_2] + k_4} \right), \quad (8)$$

where

$$\frac{k_1}{k_{-1}} = \frac{1}{2} e^{1212/kT} \quad (9)$$

which has a value of 168 at 300 K. Previous results for the values in the second term of expression (8) show that this term is also unity or greater under our experimental conditions. Hence, S ≈ 1. The results of van Veen and co-workers¹⁸ show that

$$\lambda_1 \approx C_{11} = (k_1 + k_5)[\text{N}_2] + k_2 \quad (10)$$

and hence, from expression (6),

$$\lambda_2 = (k_{-1} + k_3)[\text{N}_2] + k_4. \quad (11)$$

Thus, λ_1 is related to the initial total decay of N₂(a, v = 0) through all channels while λ_2 is related to the decay of the coupled system.

Our experiment employs an eight bit digitizer (resolution = 4×10^{-3} of full scale). Hence, the ratio of fast to slow amplitudes in our experiment is such that the slow component of the decay is much smaller than the resolution of the data acquisition system. Thus we are only able to determine λ_1 and Eq. (3) reduces to

$$[N_2(a, v = 0)]_t = [N_2(a, v = 0)]_0 e^{-(k_1 + k_s)(N_2) + k_1 t}. \quad (12)$$

This is classical first order kinetics in which the magnitude of $k_1 + k_s$ may be determined from a Stern-Volmer-type analysis.

A. Quenching by N₂

A typical two photon laser-induced fluorescence spectrum of the N₂(a-X, 0-0) band is shown in Fig. 3. All fluorescence decay experiments were performed by exciting the S-branch bandhead of this transition ($J = 7-9$). At the N₂ pressures employed in these experiments sufficient collisions are available to thermalize the rotational population of $v' = 0$ prior to quenching by other species. Though we did not attempt to observe any dependence of quenching rate on rotational level excited, we believe these experiments would not be able to detect such an effect.

The decay of N₂(a, v = 0) emission intensity as a function of time for an N₂ density of 1.3×10^{16} molecules cm⁻³ is shown in Fig. 4. The log of the emission intensity is clearly linear for in excess of three *e*-folding lifetimes in this plot (only four are practically possible). A plot of first-order rate coefficients determined as a function of N₂ density is shown in Fig. 5. The slope of this line gives the value of $k_1 + k_s$, the total quenching rate coefficient for this level by N₂. A least-squares analysis of the data gives a value for the rate coefficient of $2.2 \pm 0.1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ in excellent agreement with the results of van Veen and co-workers.¹⁸

The intercept of the line indicates a zero-pressure decay rate of 1×10^5 s⁻¹. This is approximately an order of magnitude faster than the reported lifetimes for N₂(a)⁷⁻¹⁰ and can be explained by considering diffusion out of the field of view of our detection system. Of course as the diffusion rate is inversely proportional to pressure this should result in some curvature in the plot of Fig. 5 at low pressure. However, quenching by N₂ is sufficiently rapid that the diffusion component of the decay represents only a minor contribution to the total decay rate at all but the lowest N₂ densities. No curvature can be discerned from this plot.

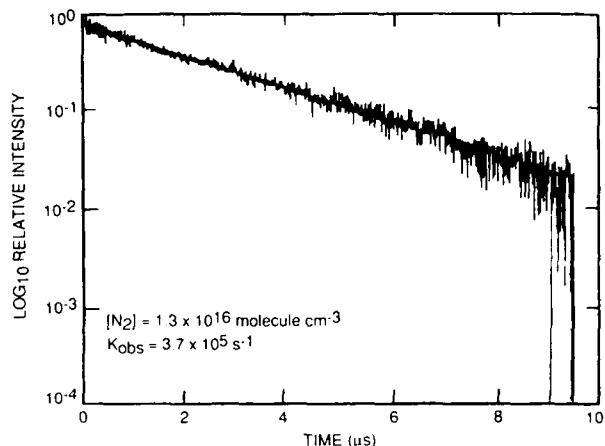


FIG. 4. Fluorescence decay of N₂(a 'II_x) following laser excitation of N₂(a, v' = 0).

B. Quenching by Ar, CO₂, H₂, O₂, and CH₄

Addition of other species to a fixed amount of N₂ enables the determination of total quenching rate coefficients for these species. In these experiments approximately 1 Torr of N₂ was employed in order to produce the N₂(a). At this pressure the decay of N₂(a) is dominated by N₂ quenching and the contribution due to diffusion is not important. First-order decay rates were determined as a function of quencher density for each species. The contribution due to quenching by N₂ was subtracted from each rate, using the rate coefficient reported above, in order to account for variations in N₂ density as the quencher density was varied. Stern-Volmer-type plots for quenching of N₂(a) by O₂, CO₂, and H₂ are shown in Fig. 6. A summary of measured rate coefficients is given in Table I.

An attempt was made to determine the quenching rate coefficient for N₂O; however, N₂O was efficiently excited by the laser at the wavelength used to excite N₂(a, v = 0). Strong VUV emission was observed in the bandpass of our detection system. Nitrous oxide is transparent at the 290 nm wavelength of our excitation laser and absorbs to a struc-

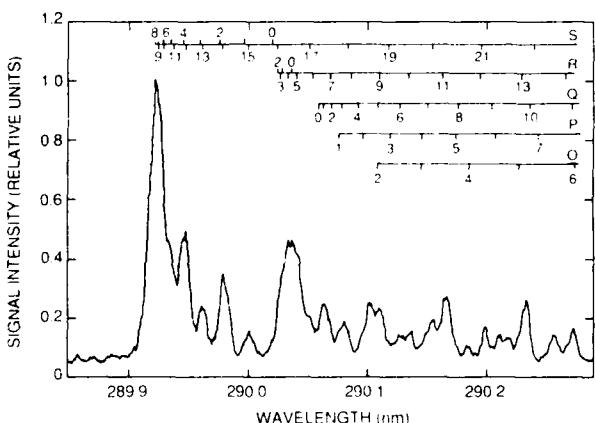


FIG. 3. Two photon laser induced fluorescence spectrum of N₂(a-X, 0-0) band.

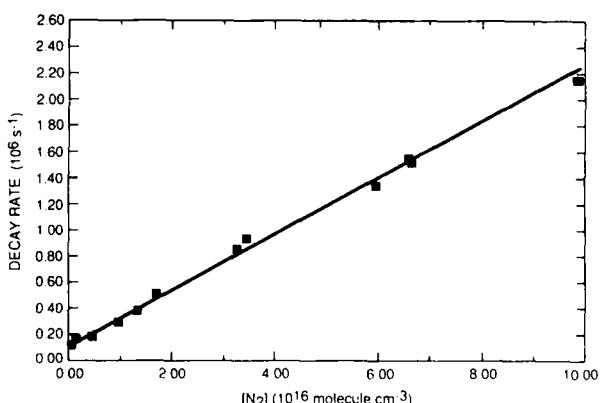


FIG. 5. Plot of first-order decay rates as a function of N₂ density. The slope of this line gives the quenching rate coefficient.

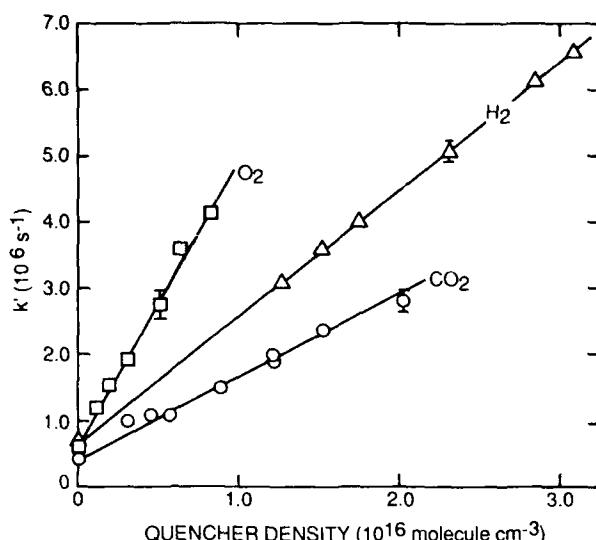


FIG. 6. Stern-Volmer plots for quenching of $N_2(a, v' = 0)$ by O_2 , H_2 , and CO_2 .

tured continuum at 145 nm (two-photon excitation). Absorption at 145 nm has been reported not to produce products which radiate in the VUV.²³ No further attempt has been made to explore this process.

C. Quenching by CO

The quenching of $N_2(a)$ by CO produced strong emission in the 130 to 190 nm bandpass of our detection system. This is due to the excitation of $CO(A^1\text{II})$ via energy transfer. Since the radiative lifetime of the $CO(A)$ state is approximately 10 ns²⁰ and the kinetic decays occur on the microsecond time scale, $CO(A)$ is in steady state during the decay and its emission can be used as a tracer for the $N_2(a)$ density. Hence, this emission can be used, exactly as the direct emission from $N_2(a)$ was employed, to obtain the quenching rate coefficient for CO. The Stern-Volmer analysis of the decay rates shown in Fig. 7 yields a rate coefficient of $2.8 \pm 0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is approximately a factor of 2 slower than observed by Kompa and co-workers.²⁰

IV. DISCUSSION

Our results for the quenching of $N_2(a, v' = 0)$ by N_2 are in good agreement with the results previously reported by van Veen and co-workers¹⁸ using two-photon excitation of

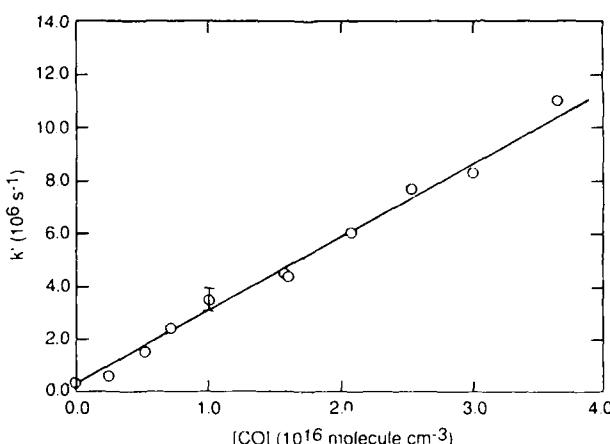


FIG. 7. Stern-Volmer plot for quenching of $N_2(a, v' = 0)$ by CO.

$N_2(a)$ in the low pressure regime. However, our rate coefficient is a factor of 2 larger than the average rate coefficient measured in our previous study for the deactivation of the a -state vibrational manifold.⁵ Our previous study employed electron beam excitation of the entire a -state and a' -state vibrational manifold. A Stern-Volmer-type analysis was employed to extract rate coefficients. That analysis is compromised by the simultaneous vibrational relaxation and $a \leftrightarrow a'$ intersystem crossing channels which accompany pure electronic relaxation. Such processes can never be fully described using the simple analytic process employed for that data. The discrepancy between the two experiments is most surely a result of additional production of the a state, via collisional feed from other states (such as a' or w) or via enhanced electron beam production. In both cases the previous study employed analytical methods which should have minimized these effects. However, factor of 2 errors are potentially possible. Our analysis of the kinetics for higher $N_2(a)$ vibrational levels should not be subject to as high an uncertainty because collisional feed from higher levels is smaller as a result of predissociation above $v = 6$.

The rate coefficient for quenching of $v = 0$ reported by Golde and Thrush¹⁵ is in much more serious disagreement with our current measurement. This is a matter of some concern since many of their subsequent measurements, some of which are in much better agreement with our results, are determined relative to the quenching rate coefficient for $v = 0$. Their study employed a discharge flow reactor in which $a-X$ emission was produced from the recombination of N atoms. The formation and loss of $N_2(a, v)$, as a function of N-atom number density and total pressure, was analyzed using a Stern-Volmer-type measurement. Their study produced a rate coefficient for the quenching of $N_2(a, v = 0)$ of $1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For higher vibrational levels (up to $v = 6$), this rate increased by greater than a factor of 10 in reasonable agreement with the scaling with v reported in our previous study.⁵

At the pressures employed in their study (1.5 to 4.5 Torr) the a' state should be strongly coupled to the a -state manifold. Rapid relaxation of the higher levels of the a state⁵ would significantly alter any distribution initially produced

TABLE I. Measured quenching rate coefficients for $N_2(a^1\Pi_g, v' = 0)$.

Species	$k_1 + k_s (10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
Ar	0.13 ± 0.01
N_2	0.22 ± 0.02
O_2	4.3 ± 0.2
CO	2.8 ± 0.2
H_2	2.0 ± 0.1
CO_2	1.30 ± 0.05
CH_4	5.2 ± 0.2

via the atom recombination process. The analysis of Golde and Thrush does not allow for the possibility of feed into the system from other electronic states or vibrational redistribution within the *a* state itself. If additional feed or vibrational redistribution was significant, the result would be a lowering of the apparent loss rate. Their study was conducted at pressures more than an order of magnitude greater than our previous study and therefore might be more subject to collisional feed processes. Later studies by Golde¹⁷ used hollow cathode discharges to excite N₂(*a'*, *v* = 0) and observed the coupling of this level to N₂(*a*, *v* = 0). This study produced a lower bound on the total relaxation of N₂(*a*, *v* = 0) by Ar of 3×10^{-12} cm³ molecule⁻¹ s⁻¹ at 295 K. This lower bound was determined using a radiative rate of 7×10^3 s⁻¹ for the *a*-*X* transition. Our measurements give a ratio of N₂/Ar quenching efficiencies of 1.6. The result of Golde and Thrush¹⁵ gave a ratio of 2.4. Subsequent revisions to the *a*-state radiative rate,²⁴ including a recent direct measurement in our laboratory²⁵ of 1.7×10^4 s⁻¹, would revise Golde's lower limit for Ar relaxation to 7.3×10^{-12} cm³ molecule⁻¹ s⁻¹. Using the ratios of rate coefficients reported above for N₂ relative to Ar, Golde's data could suggest a lower limit of 1.2 to 1.8×10^{-11} cm³ molecule⁻¹ s⁻¹ for quenching by N₂. This limit is more consistent with the laser excitation results.

Both the present study and the measurement of van Veen *et al.*¹⁸ employed direct excitation of a single state. Hence, cascade effects are not important in the kinetic analyses. The experimental configurations for each of the laser excitation experiments were quite different, yet each yielded the same rate coefficient. Thus, experimental artifacts would not appear to be an issue. The direct and more simple nature of the current experiments permits straightforward interpretation of the results.

Quenching of *v* = 0 by Ar is consistent with Golde's observation that Ar is about half as efficient as N₂.¹⁵ Our reported rate coefficient is consistent with the revised rate coefficient of Golde as presented above. The lower quenching efficiency for Ar relative to N₂ may reflect the degree to which each couples *a*(0) to *a'*(0) (*k*₁) or to other electronic manifolds (*k*₅). Our measurements cannot differentiate between the two processes.

Golde and Thrush¹⁵ reported enhanced N₂(*B*-*A*) and *a'*-*X* emission when Ar was substituted for N₂ in their experiments. They attributed the enhanced signal to an increase in the production of N₂(*B*), which may be collisionally coupled to the *a'* state. The experimental evidence is not present to separate changes in production from collisional coupling effects. However, it does highlight the degree to which the singlet-triplet distinction can be blurred near the dissociation limit. Kompa and co-workers²¹ did observe rapid rotational relaxation of N₂(*a*) by Ar, but their experiments could not probe for other relaxation channels. In future experiments we hope to test for this channel by trying to observe N₂(*B*, *v*) fluorescence following excitation of N₂(*a*).

The relaxation of *v* = 0 by H₂, CO₂, CH₄, and O₂ can probably best be characterized as dissociative quenching. The energy of this state lies well above the dissociation limit for all these species and falls within the known dissociative

optical absorption range of O₂, CO₂, and CH₄. Quenching rate coefficients for CO and CO₂ were determined by Golde and Thrush¹⁶ to be somewhat slower than observed here. However, these measurements were made in relation to their slow rate coefficient for quenching by N₂. A simple scaling of those results to reflect the revised value of *k*₁ gives rate coefficients substantially larger than gas kinetic. It is not clear whether such a simple correction is appropriate for this data. Production of O(¹D) is energetically allowed in the quenching of *v* = 0 by O₂. No enhanced emission is observed from the O₂(*B*-*X*) emission bands; however, the fluorescence yield of the bands is quite low due to predissociation effects.

The dissociation limit for CO is well above the N₂(*a*) term energy. The large increase in signal observed in CO experiments is due to the excitation of the CO (*A*'II) state which radiates in the *A*-*X* bands. The 10 ns radiative lifetime of the state results in the *A*-state functioning as a tracer for *a*, *v* = 0. Quenching by CO has recently been reexamined in a series of elegant experiments by Kompa and co-workers.²⁰ They employed REMPI detection of the CO(*A*) products to obtain branching efficiencies for formation of specific vibrational levels. Their measurement of the rate coefficient for the reaction, $6.0 \pm 1.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, is approximately a factor of 2 greater than our measurements support. Their measurement involves a careful convolution of excitation and relaxation of N₂(*a*) over the duration of the excitation/probe laser pulse to obtain the rate coefficient. This is inherently difficult and relies on a detailed understanding of the multiphoton excitation process and laser pulse profile. Our measurement employs simple pseudo-first-order kinetics to obtain the rate coefficient and consequently we believe our result should be more accurate. The measurements of relative CO(*A*, *v*) production rates in their experiments are not affected by this convolution. Their interpretation of the data does a remarkable job of describing the relaxation processes in that system.

V. CONCLUSIONS

We have determined the quenching rate coefficients for N₂(*a'*Π_g, *v* = 0) by N₂, Ar, CO, CO₂, CH₄, and H₂. The rate of quenching by N₂ is consistent with previous laser-based measurements and can be reconciled with limits made using discharge flow reactors and electron beam excitation. Relaxation by Ar is nearly as efficient as N₂. Quenching by CO results in energy transfer to form the CO(*A*'II) state. Our measurements support a value for the total quenching rate coefficient a factor of 2 smaller than the recent report of Kompa and co-workers.²⁰ Dissociation of the collision partner is thought to be the dominant pathway in the quenching of N₂(*a*, *v* = 0) by CO₂, O₂, and CH₄. All proceed at gas-kinetic rates. Future measurements will focus on the radiative lifetime of N₂(*a*, *v*) and the absolute formation efficiencies of CO(*A*, *v*) in the energy transfer from N₂(*a*).

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